

SPECIFICATION

METHOD FOR FORMING ANODIC OXIDE LAYER ON SURFACE OF
ALUMINUM OR ALUMINUM ALLOY

TECHNICAL FIELD

The present invention relates to an improvement of a method for forming an anodic oxide layer on a surface of aluminum or an aluminum alloy.

BACKGROUND ART

A method for forming a corrosion-resistant oxide layer by anodizing aluminum or an alloy thereof in an electrolytic solution such as an aqueous solution of nitric acid, sulphuric acid or chromic acid for the purpose of mainly improving corrosion resistance thereof is known as an alumite treatment. Articles subjected to the alumite treatment are widely utilized in various fields with a central focus on daily commodities such as a pan and a teakettle.

However, since an upper layer of an alumite layer is ordinarily porous, corrosion resistance is not sufficient and abrasion resistance and coloring easiness are not satisfactory. In order to solve these problems, a technique for forming a composite layer of an aluminum oxide layer and an acrylic resin composition, a technique for forming a dense composite layer in a short period of time regardless of a shape or the like of an article to be treated, and a technique for improving a coloring property are disclosed in:

Patent Document 1: JP-B No. 01-019479;

Patent Document 2: JP-A No. 02-097698; and

Patent Document 3: JP-B No. 05-014033.

However, there is a problem in that, in the case of any one of these surface treatment methods and other known alumite treatment methods, although the anodic oxide layer can easily be formed on an Al-Mn alloy, it is impossible to perform the treatment on duralumin or a die cast alloy and it is difficult to perform the treatment on other aluminum alloys.

The layer to be formed by a conventional method is restricted to have a comparably small thickness of about 30 to about 50 μm , a low hardness and the like and, accordingly, there is a given limitation upon applications thereof.

The present invention has been achieved in order to solve these problems and an object of the present invention is to provide a method for treating a surface of aluminum or an aluminum alloy which can treat various types of aluminum alloys involving not only aluminum itself, but also duralumin and a die cast alloy, can apply a thick layer of 300 to 500 μm and has a number of advantages such that the layer to be obtained has a high surface hardness, an excellent heat resistance, an antibiotic action and the like and can produce various types of aluminum materials which can be utilized in a far wide field compared with a conventional one.

The above-described object according to the present invention can be attained by performing an anodic oxidation treatment by using a bath liquid, which involves an aqueous solution containing 250 gr/l to 350 gr/l of sulfuric acid and 15 gr/l to 25 gr/l of nickel sulfate under the following conditions:

(a) Bath liquid temperature: -10°C to $+25^{\circ}\text{C}$;

(b) Voltage: DC 100 V to 200 V; and

(c) Current density: 0.5 A/dm^2 to 20 A/dm^2 .

For the sake of convenience of explanation, the above-described treatment according to the present invention is referred to as “the present treatment (1)” and a product to be obtained thereby is referred to as “present product (1)”.

The object according to the present invention can be performed more favorably by using a bath liquid in which the bath liquid to be used in the present treatment (1) is further added with a low polymerization acrylic resin composition in the range of from 280 gr/l to 320 gr/l.

For the sake of convenience of explanation, the above-described treatment according to the present invention is referred to as “the present treatment (2)” and a product to be obtained thereby is referred to as “present product (2)”.

In the present treatment (2), in order to prevent a so-called “burning (YAKE in Japanese)”, it is recommended to use a bath liquid further added with tartaric acid in the range of from 5 gr/l to 15 gr/l.

When the method according to the present invention is applied to an aluminum alloy selected from the group consisting of duralumin, an aluminum alloy for die cast and an aluminum alloy without containing Mn which are difficult to be treated by a conventional surface treatment method, it is desirable to perform an anodic oxidation treatment by using any one of the above-described bath liquids under the following conditions:

(d) Bath liquid temperature: -10°C to -5°C ;

- (e) Voltage: DC 130 V to 170 V; and
- (f) Current density: 8 A/dm² to 12 A/dm².

When the anodic oxidation treatment is performed on a surface of an aluminum alloy containing Mn, it is desirable to perform the treatment by using any one of the above-described bath liquids under the following conditions:

- (g) Bath liquid temperature: +15°C to +18°C;
- (h) Voltage: DC 130 V to 170 V; and
- (i) Current density: 8 A/dm² to 12 A/dm².

In a further desirable aspect of the present invention, after the anodic oxide layer is formed on the surface of aluminum or the aluminum alloy by any one of the above-described various types of treating methods, it is recommended to impregnate silver in the anodic oxide layer by performing a treatment using a bath liquid which involves an aqueous solution further containing 10 gr/l to 30 gr/l of silver sulfate or silver nitrate, 15 gr/l to 20 gr/l of boric acid and 1 gr/l to 2 gr/l of nickel sulfate under the following conditions:

- (j) Bath liquid temperature: +10°C to +20°C;
- (k) voltage: AC 10 V to 15 V;
- (l) current density: 1 A/dm² to 2 A/dm²; and
- (m) Current applying period: 2 minutes to 3 minutes.

For the sake of convenience of explanation, the above-described treatment according to the present invention is referred to as “the present treatment (3)” and a product to be obtained thereby is referred to as “present product (3)”.

The above-described object according to the present invention can be attained by a method for forming an anodic oxide layer on a surface of aluminum or an aluminum alloy which is characterized in that an anodic oxide layer having a thickness of 300 μm to 600 μm is formed on a surface of aluminum or an aluminum alloy by any one of the above-described various treating methods and, after the above-described silver impregnation is performed on the layer, a surface layer was removed by polishing by a thickness of 50 μm to 100 μm and, then, an ultra-hard flat surface is obtained.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is an explanatory view showing an embodiment of a device for carrying out a method for forming an anodic oxide layer on a surface of aluminum or an aluminum alloy according to the present invention; and

FIG. 2 is an enlarged cross-sectional view showing a layer portion of aluminum or an aluminum alloy subjected to the present treatment (2).

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention is specifically described with reference to drawings.

In FIG. 1, reference numeral 1 denotes an electrolyte bath; reference numeral 2 denotes an AC power supply; reference numeral 3 denotes an aluminum or aluminum alloy member to be treated by the method according to the present invention; reference numeral 4 denotes a non-consumable electrode such as carbon or graphite; and reference

numeral 5 denotes a bath liquid involving a predetermined electrolytic solution.

The present treatment (1) performs an anodic oxidation treatment by using a device as shown in FIG. 1 and an aqueous solution containing 250 gr/l to 350 gr/l of sulfuric acid, 15 gr/l to 25 gr/l of nickel sulfate as a bath liquid under the following conditions:

- (a) Bath liquid temperature: -10°C to $+25^{\circ}\text{C}$;
- (b) Voltage: DC 100 V to 200 V; and
- (c) Current density: 0.5 A/dm^2 to 20 A/dm^2 .

As described above, the present invention is entirely different from the conventional method in the point that the anodic oxidation treatment is performed under the treating conditions of a high sulfuric acid ion concentration, a low temperature and a high current density.

When a value of each of the above-described treating conditions is less than a lower limit thereof, a treating efficiency is aggravated, while, when it is more than an upper limit thereof, hardness of the layer is decreased and a desired layer can not be obtained; these are problematic.

Nickel sulfate is added for the purpose of enhancing hardness of the layer to be formed.

As for a raw material of aluminum or an aluminum alloy to form an anodic oxide layer thereon by a treatment method according to the present invention, those as described in Table 1 are mentioned.

TABLE 1			
Pure aluminum	Highly pure aluminum	99.9% or more	Type
	Industrially pure aluminum	99.7%	A1070
		99.5%	A1050
		99.0%	A1100
Aluminum alloy	Al-Cu type (containing 3.5 to 6.8% of Cu)		A2000
	Al-Mn type (containing 1.0 to 1.5% of Mn)		A3000
	Al-Si type (containing Si to a great extent)		A4000
	Al-Mg type (containing 0.5 to 5.0% of Mg)		A5000
	Al-Mg-Si type (containing about 1.0% of Mg and Si)		A6000
	Al-Zn type (containing 5.0 to 6.0% of Zn)		A7000

Further, when the method according to the present invention is applied to a hard-treating aluminum alloy which has been difficult to be treated by the conventional method such as duralumin, an aluminum alloy for die cast or an aluminum alloy without containing Mn, or any one of other aluminum alloys, a desired anodic oxide layer can be formed by using any one of above-described bath liquids and adopting the following conditions:

- (d) Bath liquid temperature: -10°C to -5°C ;
- (e) Voltage: DC 130 V to 170 V; and
- (f) current density: 8 A/dm² to 12 A/dm².

On the other hand, when the anodic oxidation treatment is performed on a surface of an aluminum alloy containing Mn, a desired anodic oxide layer can be formed by adopting the following conditions:

- (g) Bath liquid temperature: $+15^{\circ}\text{C}$ to $+18^{\circ}\text{C}$;
- (h) Voltage: DC 130 V to 170 V; and

(i) Current density: 8 A/dm² to 12 A/dm².

When the present invention to be constituted as described above is compared with a conventional method, the present invention has such advantages as described below.

(1) In the conventional method, although an anodic oxide layer can easily be formed in an Al-Mn type alloy, it is impossible to treat duralumin and a die cast alloy and it is difficult to treat other alloys.

On the other hand, according to the method of the present invention, duralumin, a die cast alloy and all types of other aluminum alloys can be treated.

(2) In the conventional method, a layer having a thickness of about 30 to about 50 μm and, even at a maximum, about 100 μm can be formed. On the other hand, according to the method of the present invention, a layer having a thickness as large as 300 to 500 μm can easily be formed.

(3) As for the layer to be formed according to the conventional method, although a surface layer thereof is hard (Vicker's hardness: 400 or less), an inside thereof is porous and hardness thereof is low.

On the other hand, as for the layer to be formed by the method according to the present invention, a surface layer thereof is hard and a Vicker's hardness is about 450 to about 500. Particularly, a lower layer is denser and harder than a surface. When a thickness of 50 to 150 μm is removed from a surface, hardness becomes 800 to 1000 in terms of Vicker's hardness.

(4) As for the layer to be formed by the method according to the present invention, heat conductivity thereof is high and is comparable with

that of copper.

(5) As for the layer to be formed by the method according to the present invention, surface thermopenetration resistance is low.

Then, when ice is placed on a tray made of aluminum or an alloy material thereof having the layer formed by the method according to the present invention, ice is melted at twice the speed of ice on an untreated tray. Therefore, for example, the tray can favorably be utilized as a tray for unfreezing a frozen food. Further, when a container made of aluminum to be heated for popcorn is subjected to the treatment according to the method of the present invention, a time period from the time of starting heating to the time of explosion of the popcorn is reduced from conventional 6 minutes to 3 minutes.

(6) As for the layer to be formed by the method according to the present invention, heat resistance is as high as about 800°C.

(7) The layer to be formed by the method according to the present invention has an antibiotic action.

Therefore, an aluminum material or an aluminum alloy material on which an anodic oxide layer is formed by the method according to the present invention can favorably be utilized in a wide field, for example, as a tray for ice-making or unfreezing, a rice cooker, a pan, a kettle, a teakettle and other cooking devices for heating, an instantaneous hot-water heater, a heat exchanger, an air-conditioner, a freezer, a refrigerator, an oil heater, a radiator, a cooling fin, an air- or water-cooled engine (acceleration of heat release), a wing of an airplane (de-icing), a heat sink for a semiconductor, a semiconductor package, a heat pipe, a bearing, various types of sliding

members, a brake shoe, a manufacturing apparatus for popcorn or ice-cream, a chassis for an electric apparatus, a casing for a motor, an electric transformer or the like.

These articles utilize a property of the present product which conducts heat efficiently.

Next, the present treatment (2) is described.

When the present treatment (2) is performed, it is characterized that the anodic oxidation treatment is performed by using a bath liquid in which the bath liquid used in the above-described present treatment (1) is further added with a low polymerization acrylic resin composition in the range of from 280 gr/l to 320 gr/l.

As for the low polymerization acrylic resin composition to be added, for example, an article containing, based on percentages, 68% of hydroxypropyl methacrylate, 10% of neopentyl glycol dimethacrylate, 19.5% of polypropylene glycol methacrylate, 1% of 1,6-hexanediol diglycidyl ether, 1% of butyl peroxyoctoate, 500 ppm of hydroquinone monmethyl ether and 0.3% of dicyandiamide is favorably used.

For the purpose of prevention of "burning", it is recommended to further add tartaric acid to the above-described bath liquid in the range of from 5 gr/l to 15 gr/l.

By such present treatment (2) as described above, an oxide layer which is a composite of aluminum oxide and the acrylic resin composition is formed. Namely, a metallurgical porous oxide layer and the acrylic resin composition are acid-ionized and polymerized therebetween and, then, form a tough and dense composite layer, to thereby enhance corrosion resistance

and abrasion resistance to a great extent. Further, since the layer is formed while drawing out a gas in a pin-hole portion, the layer has characteristics such that pin-holes are small in number and, further, since the oxide layer is slowly formed at a low temperature, it is excellent in density and, since the layer is hard to be peeled off, it can be subjected to machining and a surface roughness thereof remains unchanged.

The anodic oxide layer obtained by the present treatment (2) is now explained with reference to an enlarged cross-sectional view showing a layer portion of FIG. 2.

In FIG. 2, reference numeral 21 denotes an aluminum material or aluminum alloy material as a base metal; reference numeral 22 denotes an anodic oxide layer; reference numeral 23 denotes a barrier layer; reference numeral 24 denotes a porous layer portion; reference numeral 25 denotes an acrylic resin composition layer portion.

The anodic oxide layer 22 involves a barrier layer 23 formed on the aluminum material or aluminum alloy material 21, a porous layer portion 24 formed thereon and an acrylic resin composition layer portion 25 which is impregnated inside the porous layer and fixed therein. By these two layer portions 24, 25, a tough and dense composite layer is formed. As for the composite layer, as a portion thereof is closer to the barrier layer 23, the portion comes to have a higher hardness and becomes denser and, as described below, by removing a region close to a surface by machining, the surface having a further higher hardness can be obtained.

Next, the present treatment (3) is described.

When the present treatment (3) is performed, after the anodic oxide

layer is formed on a surface of an aluminum or aluminum alloy by any one of the above-described various types of treating methods, it is characterized in that silver is impregnated in the anodic oxide layer by performing an anodic oxidation treatment using a bath liquid which involves an aqueous solution further containing 10 gr/l to 30 gr/l of silver sulfate or silver nitrate, 15 gr/l to 20 gr/l of boric acid and 1 gr/l to 2 gr/l of nickel sulfate under the following conditions:

- (j) Bath liquid temperature: +10°C to +20°C;
- (k) Voltage: AC 10 V to 15 V;
- (l) Current density: 1 A/dm² to 2 A/dm²; and
- (m) Current applying period: 2 minutes to 3 minutes.

Decrease of a silver ion concentration along a progress of treatment is covered by replenishment of silver sulfate or silver nitrate.

Boric acid is added mainly for adjustment of electric conductivity of the electrolytic solution.

When the voltage is less than 10 V, a treatment efficiency becomes deteriorated, while, when it is over 15 V, deposition of silver is unduly rapidly performed and the oxide layer can not sufficiently be impregnated inside the porous layer and uneven coloring, peeling or the like tends to be generated.

In a same manner, when the temperature of the electrolytic solution is less than +10°C, the treatment efficiency is aggravated, while, when it is more than +20°C, uneven coloring tends to be generated.

By such present treatment (3) as described above, a silver ion is deeply impregnated inside the porous anodic oxide layer (electrolytically

impregnated by alternating voltage) and, then, combines with aluminum oxide, to thereby form a tough dense composite layer. For this account, the surface layer excellent in the heat conductance, the corrosion resistance, the abrasion resistance, the antibiotic action and the like can be formed. Further, the surface layer has the electric conductance and has a small coefficient of friction and a small color change in time. Further, the layer has effects such as far-infrared emission, removal of static electricity and the like.

Such present treatment (3) can be performed on all types of aluminum material and aluminum alloy material and can form a thick layer having various types of excellent characteristics as described above on the surface thereof.

In the present invention, further, an anodic oxide layer having a thickness of 300 μm to 600 μm is formed on a surface of aluminum or an aluminum alloy by the above-described various types of treating methods and, then, further, the above-described silver impregnation is performed and, thereafter, a surface layer is removed by polishing in a depth of from 50 to 100 μm from the surface and, subsequently, an aluminum material or aluminum alloy material having a ultra-hard smooth surface can be provided.

Namely, as for the layer to be formed by the method according to the present invention, a surface hardness is high and is about 450 to about 500 in terms of Vicker's hardness. Particularly, a lower layer is denser than the surface and is higher in hardness. Then, when 50 to 150 μm from the surface is removed, the aluminum material or aluminum alloy material

having an ultra-hardness of 800 to 1000 in terms of Vicker's hardness and a smooth face can be obtained.

Hereinafter, various types of characteristics of the present product are shown.

In Table 2, characteristics of products on which the present treatment has been applied are shown by materials.

TABLE 2

Material type	Conventional alumite	Present product						
		Thickness μ	Silver impregnation	Hardness	Insuration	Heat conduction	Antibiotic property	Slipperiness
AL00	**	60	Possible	450		Substantioally increased	Possessing	2.5
AL10	**	60	Possible	450		The same as above.	The same as above.	2.5
AL20	*	60	Possible	450		The same as above.	The same as above.	2.5
AL30	**	60	Possible	450		The same as above.	The same as above.	2.5
AL40	**	60	Possible	450		The same as above.	The same as above.	2.5
AL50	***	100	Possible	450		The same as above.	The same as above.	2.5
AL60	***	100	Possible	450		The same as above.	The same as above.	2.5
AL70	**	60	Possible	450		The same as above.	The same as above.	2.5
AL80	**	60	Possible	450		The same as above.	The same as above.	2.5
AC2	**	60	Possible	370		The same as above.	The same as above.	
AC3	**	60	Possible	370		The same as above.	The same as above.	
AC4	**	60	Possible	370		The same as above.	The same as above.	
AC7	**	60	Possible	370		The same as above.	The same as above.	
ADC1	*	30	Possible	370		The same as above.	The same as above.	
ADC2	*	30	Possible	370		The same as above.	The same as above.	
ADC3	*	30	Possible	370		The same as above.	The same as above.	
ADC4	*	30	Possible	370		The same as above.	The same as above.	

Conventional alumite marks:

*: Impossible to be machined :

** : Difcult to be machined

***: Easy to be machined

As for the heat conductivity, when that of silver is taken as 1, that of the present product is 0.9; that of copper is 0.94; and that of aluminum is 0.53. Therefore, the heat conductivity of the present product is higher than that of aluminum as a base metal and is comparable with that of copper.

This property shows that the present product is excellent as a raw material for various types of heat transfer members, diathermal members, heat releasing members.

As for the hardness (Hv), that of aluminum is 80, that of stainless steel is 200, that of the present product is 450. Accordingly, the hardness of the present product is more than twice that of stainless steel.

By making use of this property, various types of parts which require abrasion resistance such as a gear, a roller, a guide rail, a shaft, a bearing, a brake shoe, a cylinder liner and piston, a valve, a piston pump and a screw pump can be produced.

As for the upper temperature limit (°C), that of polytetrafluoroethylene is 260°C; that of aluminum is 660°C; and that of the surface layer of the present product is 800°C.

By making use of this property, the present product can provide a flame-retardant shutter, heat-resistant wall material and the like.

When the abrasion resistance test was performed, it has been found that an abrasion amount of the present product was one tenth the abrasion amount of ordinary hard-type alumite.

Namely, the abrasion test was conducted by arranging a test piece to be in a rotating side and a resin-type oil-less bearing material in a fixing

side. Testing conditions were as follows: vibration speed: 1m/s; face pressure: 20 kgf/cm²; and test duration: 3 hours. As a result, the abrasion amount of the hard-type alumite was 2.5 μ m while that of the present product was 0.25 μ m.

When a burning-down test was conducted, the surface pressure of the burning-down of the present product was twice that of the ordinary hard-type alumite.

Namely, as for the burning-down test, a wear coefficient was measured by arranging the test piece to be in a rotating side and a resin-type oil-less bearing material in a fixing side. A load at the time the wear coefficient showed an abrupt increase was evaluated as a critical load of the burning-down. The critical load of the ordinary hard-type alumite was 160 kgf/cm², while that of the present product was 320 kgf/cm².

When a progress of a crack was measured by a high-temperature test, the present product was small in the number of initial cracks and also small in the number of cracks increased by heating, compared with TUFRAM (trade name: a product prepared by subjecting hard-type alumite to a sintering treatment and, then, impregnating the resultant alumite with polytetrafluoroethylene).

Namely, when the number of cracks in a measuring area of 16.4 mm² in a flat portion was measured, those of the present product were 0 before heating and 12 after heating, while those of the TUFRAM were 263 before heating and 321 after heating.

An antibiotic activity test was conducted. Details thereof are described below.

(a) Specimen:

Specimen 1: aluminum: a surface-treated article subjected to a silver-impregnating treatment according to the present invention (surface layer thickness: 25 μm)

Specimen 2: aluminum: non-treated article

(b) Purpose of test

An antibiotic force test is performed on the specimens.

(c) Outline of test

Specimens (hereinafter, referred to also as "samples") were inoculated with *Escherichia coli*, *Staphylococcus aureus*, *Vibrio parahaemolyticus* and *Salmonella enteritidis* by means of dropping respective bacterial liquids thereon and, after stored for 24 hours at 35°C, the number of viable bacteria in each of the samples was counted.

(d) Testing method

(i) Bacteria provided for testing

Escherichia coli IFO 3301;

Staphylococcus aureus IFO 12732;

Vibrio parahaemolyticus RIMD 2210100; and

Salmonella enteritidis IFO 3313.

(ii) Culture medium

NA culture medium: ordinary agar culture medium;

NB culture medium: ordinary bouillon culture medium added with 0.2% of meat extract; and

SA culture medium: reference agar culture medium.

(iii) Adjustment of bacterial liquid

Bacteria used in the test were inoculated in an NA culture medium at 35°C and incubated for 16 to 24 hours and, thereafter, again inoculated in an NA culture medium at 35°C and incubated for 16 to 20 hours. After such incubation, the resultant fungus bodies of bacteria used in the test were dispersed in a 1/200 concentration NB culture medium and appropriately diluted in the 1/200 concentration NB culture medium such that the number of the fungus bodies come to be 10^5 to 10^6 , to thereby prepare a bacterial liquid. On this occasion, the NA culture medium and the 1/200 concentration NB culture medium which have been added with 3% of table salt were used for *Vibrio parahaemolyticus* RIMD 2210100.

(iv) Adjustment of sample

A testing face of the sample was lightly wiped with absorbent cotton containing 99.9% (v/v) ethanol and, then, sufficiently dried.

(v) Testing operation

0.5 ml of a bacterial liquid was dropped on a sample and, then, after attached with a polyethylene layer, stored for 24 hours at 35°C and, thereafter, the number of viable bacteria was counted. Further, 0.5 ml of the bacterial liquid was dropped in a plastic petri dish and, then, after attached with a polyethylene layer, allowed to be a reference sample and, thereafter, subjected to testing in a same manner as in the above. A parallel measurement was conducted three times.

iv) Measurement of number of viable bacteria

Viable bacteria were washed out of each sample by using 9.5 ml of a SCDLP culture medium (available from Nihon Pharmaceutical Co., Ltd.). The resultant washed-out liquid was subjected to a measurement of the

number of viable bacteria by a pour plate culture method (incubated for 48 hours at 35°C) using an SA culture medium, to thereby determine the number thereof per sample. On this occasion, the SCDLP culture medium and the SA culture medium which have been added with 3% of table salt were used for *Vibrio parahaemolyticus*.

(e) Test result

The measuring results of the number of viable bacteria of the bacteria used in the test which has been dropped on the sample are as shown below in Table 3.

TABLE 3

Bacteria used in test ^{*1}	Storage time	Sample	Number of viable bacteria (per sample)		
			Test-1	Test-2	Test-3
Escherichia coli	At start-up time	Reference ^{*2}	2.2×10^5	2.5×10^5	1.5×10^5
	After stored for 24 hrs. at 35°C	Specimen 1)	<10 ^{*3}	<10	<10
		Specimen 2)	5.6×10^6	1.0×10^7	1.9×10^4
		Reference ^{*2}	1.8×10^7	1.7×10^7	2.4×10^7
Staphylococcus aureus	At start-up time	Reference ^{*2}	4.6×10^5	3.4×10^5	4.4×10^5
	After stored for 24 hrs. at 35°C	Specimen 1)	3.5×10^3	<10	<10
		Specimen 2)	1.1×10^4	1.2×10^3	1.0×10^5
		Reference ^{*2}	3.0×10^6	6.2×10^6	4.6×10^5
Vibrio parahaemolyticus	At start-up time	Reference ^{*2}	2.8×10^5	3.5×10^5	3.4×10^5
	After stored for 24 hrs. at 35°C	Specimen 1)	<10	20	2.6×10^2
		Specimen 2)	7.5×10^6	3.5×10^7	4.2×10^7
		Reference ^{*2}	4.9×10^5	6.5×10^6	4.7×10^5
Salmonella enteritidis	At start-up time	Reference ^{*2}	2.5×10^5	2.2×10^5	2.4×10^5
	After stored for 24 hrs. at 35°C	Specimen 1)	<10	<10	<10
		Specimen 2)	80	3.1×10^2	3.2×10^2
		Reference ^{*2}	1.1×10^7	1.7×10^7	8.1×10^5

In Table 4 below, performances of treated articles (Tough-coat: trade name) according to the above-described patent documents 1 and 2 and another treated article (Metal-coat: trade name) according to the above-described patent document 3 are shown as comparable examples. These performances are by far excellent compared with known articles but are inferior to the above-described present product.

TABLE 4 1/2

Sample No	Color exhibiting state	Surface irregularity	Observation of crack			Treated film thickness μ			
			Flat portion	Curved portion	evaluation	Outer surface		Inner surface	
						Flat portion	Curved portion	Flat portion	Curved portion
No.1 Hard-type alumite 20 μ	Silver	Although there is a fine dent of 1 mm or less, it is flat. Ex.	Many	Few & narrow	Bad	25.0	22.7	22.5	22.5
No.2 Tough-coat 20 μ	Slightly dark silver	The same as above.	Few	Few & narrow	Excellent	26.7	22.8	21.5	22.6
No.3 Tough-coat 20 μ	Dark silver	The same as above.	Somewhat many	Few but wide	Not Ex.	44.7	37.8	37.5	42.4
No.4 Metal-coat silver 25 μ	Dark brownish-red	The same as above.	None	Few & narrow	Excellent	17.5	16.3	14.5	15.5
No.5 Metal-coat silver 50 μ	Light brownish-red	The same as above.	Somewhat many	Few & narrow	Not Ex.	44.2	38.4	33.6	38.4
No.6 Metal-coat copper 25 μ	Dark brass yellow	The same as above.	None	Few & narrow	Excellent	14.8	13.9	13.6	13.8
No.7 Metal-coat copper 50 μ	Light brass yellow	The same as above.	Somewhat many	Few but wide	Not Ex.	50.0	42.1	42.5	45.0
No.8 Electroless nickel 5 μ	Slightly dark silver	Large projections of about 10 mm can be found in a plurality of places. Not Ex.	None	None	Excellent	5.5	6.5	5.6	5.7
No.9 Degreasing treatment only	silver	There are many projections and recesses in streaks. Not Ex.	None	None	Excellent	-	-	-	-

TABLE 4 2/2

Sample No	Hardness		Progress of number of cracks						Discharge d gas	Comprehensiv e evaluation
	Hardness	Evaluation	150℃	200℃	250℃	Average	Evaluation			
No.1 Hard-type alumite 20 μ	339	C	261	267	260	263	D	D	Extremely small	D
			23	45	105	58	D			
No.2 Tough-coat 20 μ	483	A	18	7	7	11	B	B	The same as the above	B
			22	13	38	24	B			
No.3 Tough-coat 20 μ	445	B	37	52	53	47	C	C	The same as the above	C
			37	72	90	66	D			
No.4 Metal-coat silver 25 μ	464	A	0	0	0	0	A	A	The same as the above	A
			2	13	20	12	B			
No.5 Metal-coat silver 50 μ	473	A	39	49	28	39	B	C	The same as the above	C
			35	75	47	52	D			
No.6 Metal-coat copper 25 μ	483	A	0	0	0	0	A		The same as the above	A
			17	7	21	16	B			
No.7 Metal-coat copper 50 μ	483	A	33	43	50	42	C	C	The same as the above	C
			35	74	79	63	D			
No.8 Electroless nickel 5 μ	302	C							The same as the above	C
No.9 Degreasing treatment only	78.5	D							The same as the above	C

Upper column: The number of cracks at an initial stage
(per 16.4 dm²)

Lower column: Increment of cracks generated by the test

A:0~10

B:11~30

C:31~50

D:51~

INDUSTRIAL APPLICABILITY

Since the present invention is constituted as described above, according to the present invention, such action effects as described below can be achieved.

(1) In the conventional method, although an anodic oxide layer can easily be formed in an Al-Mn type alloy, it is impossible to treat duralumin and a die cast alloy and it is difficult to treat other alloys.

On the other hand, according to the method of the present invention, duralumin, a die cast alloy and all types of other aluminum alloys can be treated.

(2) In the conventional method, a layer having a thickness of about 30 to about 50 μm and, even at a maximum, about 100 μm can be formed. On the other hand, according to the method of the present invention, a layer having a thickness as large as 300 to 500 μm can easily be formed.

(3) As for the layer to be formed according to the conventional method, although a surface layer thereof is hard (Vicker's hardness: 400 or less), an inside thereof is porous and hardness thereof is low.

On the other hand, as for the layer to be formed by the method according to the present invention, a surface layer thereof is hard and a Vicker's hardness is about 450 to about 500. Particularly, a lower layer is denser and harder than a surface. When a thickness of 50 to 150 μm is removed from a surface, hardness becomes 800 to 1000 in terms of Vicker's hardness.

(4) As for the layer to be formed by the method according to the present invention, heat conductivity thereof is high and is comparable with

that of copper.

(5) As for the layer to be formed by the method according to the present invention, surface thermopenetration resistance is low.

Then, when ice is placed on a tray made of aluminum or an alloy material thereof having the layer formed by the method according to the present invention, ice is melted at twice the speed of ice on an untreated tray. Therefore, for example, the tray can favorably be utilized as a tray for unfreezing a frozen food. Further, when a container made of aluminum to be heated for popcorn is subjected to the treatment according to the method of the present invention, a time period from the time of starting heating to the time of explosion of the popcorn is reduced from conventional 6 minutes to 3 minutes.

(6) As for the layer to be formed by the method according to the present invention, heat resistance is as high as about 800°C.

(7) The layer to be formed by the method according to the present invention has an antibiotic action.

Therefore, an aluminum material or an aluminum alloy material on which an anodic oxide layer is formed by the method according to the present invention can favorably be utilized in a wide field, for example, as a tray for ice-making or unfreezing, a rice cooker, a pan, a kettle, a teakettle and other cooking devices for heating, an instantaneous hot-water heater, a heat exchanger, an air-conditioner, a freezer, a refrigerator, an oil heater, a radiator, a cooling fin, an air- or water-cooled engine (acceleration of heat release), a wing of an airplane (de-icing), a heat sink for a semiconductor, a semiconductor package, a heat pipe, a bearing, various types of sliding

members, a brake shoe, a manufacturing apparatus for popcorn or ice-cream, a chassis for an electric apparatus, a casing for a motor, an electric transformer or the like.